

Technetium Measurements by Accelerator Mass Spectrometry at LLNL

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Technetium measurements by accelerator mass spectrometry at LLNL

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Abstract

Technetium-99 is a long-lived, high-abundance fission product which has been widely distributed in the environment through atmospheric testing, the nuclear fuel cycle, and nuclear medicine. It has a high potential for migration in the environment as the pertechnetate anion. At the Center for Accelerator Mass Spectrometry, methods are being developed for the detection of this radionuclide by accelerator mass spectrometry (AMS), including extraction from environmental samples, concentration and purification of the ⁹⁹Tc, conversion to a form appropriate for AMS analysis, and quantification by AMS. Besides interference from the stable (though relatively rare) atomic isobar ⁹⁹Ru, the detection of ⁹⁹Tc by AMS presents some technical challenges which are not present for the other radionuclides typically measured by AMS. These challenges are related to the lack of a stable Tc isotope. Here we present the status of our ⁹⁹Tc methods including discussion of interferences and sensitivity, and recent results for environmental samples and the IAEA reference material IAEA-381, Irish Sea water. Sensitivity is presently ~10 μBq (~1×10⁸ atoms) per sample, limited primarily by ⁹⁹Ru introduced from process chemicals, and precision/reproducibility is ~15-25%.

1. Introduction

Technetium-99 is a long-lived (2.1×10^5 a), high-abundance (6%) fission product which has been widely distributed in the environment through atmospheric testing, the nuclear fuel cycle, and nuclear medicine. It has a high potential for migration in the environment as the pertechnetate anion. This radionuclide is a weak beta emitter which is difficult to measure at low levels by decay counting methods. A number of mass spectrometric methods have been developed to address needs for low-level ^{99}Tc measurements, including thermal ionization mass spectrometry (TIMS),¹⁻³ inductively-coupled plasma mass spectrometry (ICP-MS),⁴⁻⁶ resonance ionization mass spectrometry (RIMS).^{7,8} More recently, the feasibility of accelerator mass spectrometry (AMS) for ^{99}Tc measurements has been demonstrated.⁹⁻¹¹

Technetium-99 AMS presents technical challenges which are not encountered for the other radionuclides typically measured by AMS. These challenges relate to the lack of a stable technetium isotope.^{9,10} In AMS measurements of other long-lived radionuclides, stable isotopes of the element of interest implicitly fill several important roles such as chemical carrier, sample matrix, internal yield monitor, and instrument normalization. In the case of ^{99}Tc , these roles must be filled by some combination of other elements and other (radioactive) technetium isotopes. In the present work niobium (sample matrix and instrument normalization) and $^{95\text{m}}\text{Tc}$ (chemical yield monitor) are used.

A further challenge in mass spectrometric measurements of ^{99}Tc is background from the isobaric interference ^{99}Ru . AMS provides a significant advantage in this regard in that the high energy of the resulting ions allows the use of nuclear-physics type particle identification for the post-spectrometer rejection of this and other interferences. For the energies attainable with the CAMS spectrometer, a rejection of ^{99}Ru by up to two orders of magnitude is obtained.

2. AMS measurements of technetium-99 at LLNL

Sample Preparation

Our present samples are primarily aqueous samples or simple leachates of soils. Aqueous samples or leachates are reduced in volume to ~100 mL (small samples are diluted to ~100 mL) and boiled with peroxide to fully oxidize technetium and to destroy organics. Persulfate is added if necessary to generate a more aggressive oxidation. Calcium and barium are added for samples with high levels of dissolved salts to precipitate major matrix components. Supernatants are filtered at 0.2 μm and loaded onto a column containing 2 mL of a technetium-specific resin (Eichrom TEVA-Spec). Following rinsing with 0.1 and 1 M nitric acid, Tc is eluted with 15 mL of 8 M nitric into a teflon vial.

Niobium is added to the eluent as peroxoniobium¹² (2 mg total Nb in concentrated peroxide/nitric acid solution). The vial is capped with a flow-through lid and the samples are dried under a dry nitrogen flow at low temperature on a hot plate. Once dried, the niobium oxide pellet is transferred to a small borosilicate test tube and baked at 400° C for ~1 hr. The pellet is then crushed to improve sample homogeneity, and pressed into a standard LLNL aluminum AMS sample holder.

Technetium recovery is monitored using ^{95m}Tc as a tracer. Our ^{95m}Tc stock was extracted from a spallation target and contains high ⁹⁹Tc concentrations. To avoid this contamination in samples prepared for AMS analyses, separate splits were taken for recovery measurements. An alternative source of ^{95m}Tc, reported to produce ⁹⁹Tc-free material,¹³ is alpha bombardment of ⁹³Nb, which we plan to employ for future measurements. Results of the tracer work show typically high recovery (> 90%) for aqueous samples and mixed results for soil leachates, depending on the soil type. Transfers of pertechnetate onto and off of the column, and ultimately to the final sample pellet, are consistently quantitative.

AMS Measurement

AMS measurements are performed using the LLNL AMS spectrometer (Figure 1).^{14,15} Negative ions are produced in the cesium sputter source¹⁶ and accelerated to 40 kV. $^{99}\text{Tc}^{16}\text{O}$ and $^{93}\text{Nb}^{16}\text{O}$ ions are quasi-simultaneously injected into the accelerator (~ 3 Hz cycle; 1 ms $^{93}\text{Nb}^{16}\text{O}$; 300 ms $^{99}\text{Tc}^{16}\text{O}$). The high energy spectrometer is set to select $^{99}\text{Tc}^{13+}$ ions at 125 MeV energy, and $^{93}\text{Nb}^{13+}$ current is measured in an off-axis Faraday cup located after the first high energy analyzing magnet. Count rates are $\sim 5 \text{ s}^{-1}$ for samples containing 100 fg ^{99}Tc , and samples can be measured for >30 min, for a total efficiency $\sim 1\text{-}2 \times 10^{-5}$ detected counts per sample atom. Extracted $^{93}\text{Nb}^{16}\text{O}$ currents are typically 1-2 μA , and stripping yield in the 13+ charge state is 4-5%.

Ion counting is performed using a gas ionization detector filled to 110 Torr with P10 (90% argon, 10% methane). Differential energy loss is measured in 3 anodes. Two dimensional spectra (first anode v. third anode), gated on the second anode, are used for particle identification. ^{99}Ru and ^{99}Tc peaks are not fully resolved at the energies available with the 10 MV LLNL accelerator. Separate Tc and Ru windows are placed on the spectra, with $\sim 85\%$ of the Tc events and $\sim 25\%$ of the Ru events occurring within the Tc window. For quality control, a third window is included to monitor for Mo events which are occasionally evident in the spectra. The detected Mo rate is nearly always negligible compared to the Ru rate for environmental samples. Corrected Tc, Ru, and Mo counts are determined analytically from the gated events. Counting uncertainties and systematic uncertainties in the deconvolution (caused by small gain shifts in the detector) are included in the corrected results. The parameters (the fractions of Tc, Ru, and Mo events in each cut) for the deconvolution are determined by repeatedly running blanks, high activity Tc standards, and spiked Ru samples as part of the measurement protocol.

Ratios of Tc counts to Nb integrated charge, corrected for electronics deadtime and ^{99}Ru background, are computed for each sample. This ratio is converted to total sample ^{99}Tc by

normalizing to the same ratio as measured for ^{99}Tc standards, then multiplying by the amount of Nb carrier solution added.

3. Results

We have measured ^{99}Tc in soil leachates and fresh and sea water samples. Sensitivity of 10-20 fg is typical for each sample type, and low-level standards containing 20 fg ^{99}Tc are readily measureable above background. Three difficulties have been encountered in these measurements. These are: variability in the measured ratios; matrix material which is not removed during sample preparation; and relatively high ruthenium levels in some samples.

To evaluate our methods, we measured ^{99}Tc concentrations in the reference material IAEA-381, Irish Sea water. A ^{99}Tc activity of 217 ± 11 mBq/kg was reported in the IAEA report on this material.¹⁷ Figure 2 shows the results for a set of 20 IAEA-381 aliquots which were included as part of a set of ~120 environmental samples (plus associated blanks, standards, and tests) measured over a 3 day period. The average of the AMS results is 190 mBq/kg, with a standard deviation of $\pm 14\%$. No correction for chemical recovery is included in these results. If the two most extreme outliers are removed, the average remains 190 mBq/kg and the standard deviation drops to $\pm 10\%$.

The variability observed in the IAEA-381 results is typical of that seen in samples and standards. The source of this sample-to-sample variation is time-dependence in the Tc/Nb ratio measured for an individual sample over the course of the measurement. This time-dependence has also been reported by the AMS group at the Australian National University, where Tc/Rh ratios are measured.¹⁸ This variability may be caused by differences in the sputtering rates of Tc and Nb or sample inhomogeneity. The effect of this time-dependence can be reduced by integrating the measurement over a longer time, and assuring that the integration time is as similar as possible for different samples. Presently this represents the major limitation to our measurements.

Fresh water samples from 1-200 mL have been measured with ~15 fg sensitivity. Based on the relative ease of sample preparation for water samples, samples as large as 1 L should be easily measureable with an expected sensitivity of ~0.01 mBq/kg (~0.3 fCi/L).

Soil leachates have been measured in arid soils for samples up to 250 g. A difficulty in the largest samples (and in some ~100 mL freshwater samples) is the presence of significant quantities (milligrams) of non-volatile material (presumably soluble salts) which are not fully removed by the sample chemistry. For quality control, each pellet is weighed after baking. The primary effect of this material is dilution of the niobium and technetium, resulting in low or undetectable signals — no interferences from this material are observed in the detector spectra. Since it is not known how this dilution might affect the measured Tc/Nb ratio, these samples are flagged as suspect. Efforts to fully identify and remove this remaining material is ongoing. Initial experience shows that precipitation steps using calcium and barium, combined with additional rinse volumes of the column prior to elution, can reduce this material to acceptable levels in most cases.

In a recent depth profile of an arid soil using 60-220 g aliquots, the average and standard deviation of 18 baseline samples was 1 ± 11 fg per aliquot (Figure 3). Surface activity, presumably from fallout, of 0.1-2 mBq/kg was readily measurable above background. A near surface sample was also readily measureable above background, with a measured value of 15 fg ^{99}Tc in a 120 g aliquot. These results are still preliminary, but they demonstrate the sensitivity of the method.

3. Conclusions

AMS is a rapid, sensitive method for ^{99}Tc measurements in a variety of sample types. Low femtogram sensitivity (similar for instance to TIMS³) is obtained through high detection efficiency, MeV ion energies which allow unambiguous measurement and subtraction of ^{99}Ru isobaric interferences, and molecular dissociation during acceleration. The relatively simple

sample preparation and high throughput of AMS analyses will allow future studies which require both high sensitivity and large data sets.

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Figure Captions

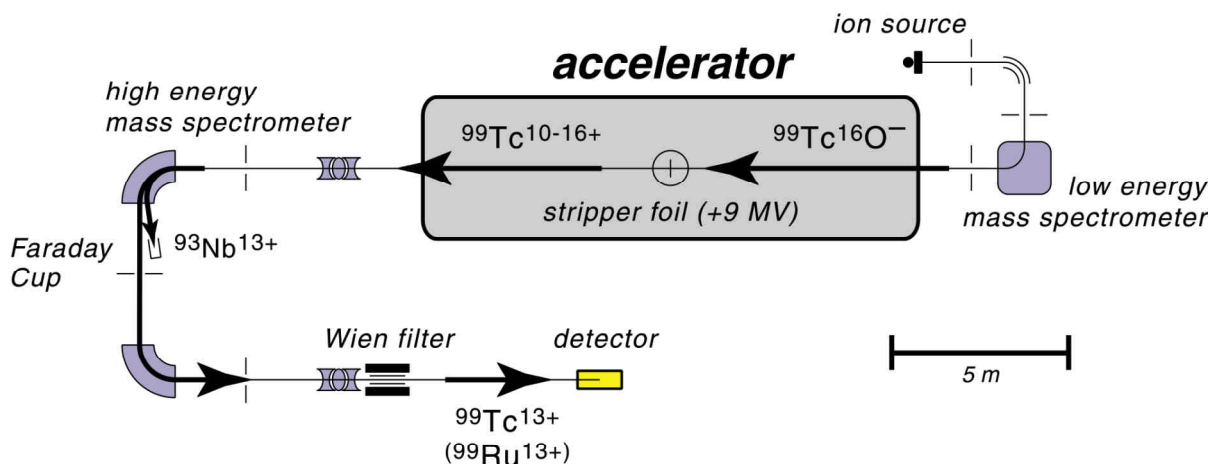


Figure 1 Accelerator mass spectrometry measurements of ^{99}Tc at LLNL. Samples are prepared as technetium oxide in a niobium oxide matrix, then placed in the Cs-sputter source. The resulting $^{99}\text{Tc}^{16}\text{O}^-$ and $^{93}\text{Nb}^{16}\text{O}^-$ ions are accelerated to 9 MV, then passed through a thin carbon foil where the molecules are dissociated and outer electrons are stripped, producing multiply charged positive ions. The high energy spectrometer is set to accept $^{99}\text{Tc}^{13+}$ ions, which are transported to the gas ionization detector following rigidity and velocity analysis. $^{93}\text{Nb}^{13+}$ currents are measured in an off-axis Faraday cup following the first high energy magnet.

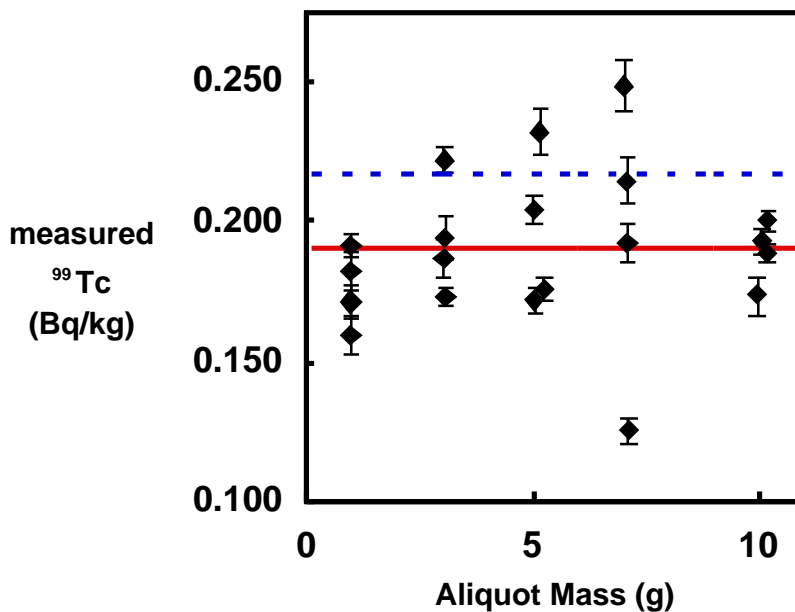


Figure 2. AMS measurements of ^{99}Tc in IAEA-381, Irish Sea Water. For comparison, the IAEA report on this material lists a single reported ^{99}Tc concentration of 217 ± 11 mBq/kg (dashed line) (Povinec, et al. 1999). For the present work, 20 aliquots (1-10 g) were prepared as described in the text, then analyzed with other samples over the course of 3 days. The average for all values (solid line) is 190 mBq/kg with a standard deviation of $\pm 14\%$. When the two most extreme outliers are excluded, the average remains 190 mBq/kg, and the standard deviation drops to $\pm 10\%$. These AMS results should be considered preliminary.

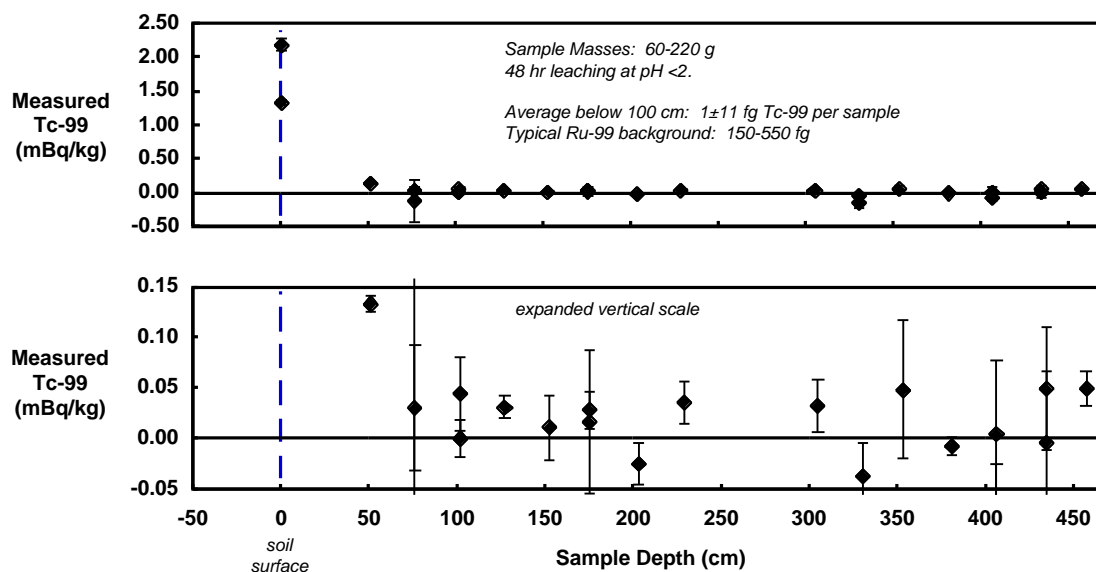


Figure 3. AMS measurements of ^{99}Tc in arid soils. Measurement vertical distribution of ^{99}Tc in an arid soil. Samples, 60-220 g, were leached for 48 h at $\text{pH} < 2$, and the leachate was prepared and measured as described in the text. The average measured ^{99}Tc for samples below 100 cm depth is 1 fg per sample with a standard deviation of ± 11 fg.

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